RESTRICTED ROTATION IN SOME AROMATIC AMINES

BY

NORMAN KARL SUNDHOLM
B. Chem., University of Minnesota, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS
1944

RESTRICTED ROTATION IN SOME AROMATIC AMINES

BY

NORMAN KARL SUNDHOLM
B. Chem., University of Minnesota, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1944

URBANA, ILLINOIS
1944

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0367

ACKNOWLEDGMENT

The author desires to express his appreciation to Professor Roger Adams for initiating this problem and for his helpful suggestions and encouragement during its development. He also desires to thank the Allied Chemical and Dye Corporation for the fellowship held during the second semester of the year 1941-1942 and during the period from June, 1943, to February, 1944, and to thank the New York Community Trust for the fellowship held during the year 1942-1943.

RESTRICTED ROTATION IN SOME AROMATIC AMINES

Introduction

This investigation is a continuation of work done in this Laboratory[1,2,3] on restricted rotation of the carbon-nitrogen bond in substituted anilines and naphthylamines. The interference effect of some electronegative groups ortho to the amino group has been observed.

Discussion of Results

The following compounds were synthesized, resolved, and their half-life periods in a suitable boiling solvent determined: N-succinyl-1-methylamino-2,4-dimethyl-6-bromobenzene, 3.2 hours in *n*-butanol; N-succinyl-1-methylamino-2,4-dimethyl-6-iodobenzene, 20 hours in *n*-butanol; N-succinyl-1-methylamino-2,4-dimethyl-6-nitrobenzene, 36 minutes in methyl acetate; N - succinyl - 1 - methylamino - 2 - methyl - 4,6 - dibromobenzene, 1.1 hours in *n*-butanol; N-succinyl-1-isopropylamino-2,4-dimethyl-6-bromobenzene, 225 hours in *n*-butanol. N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene and N-succinyl-1-amino-2,4-dimethyl-6-iodobenzene could not be resolved.

The chloro, bromo, and nitro groups show smaller interference effects in these amines than they do in the biphenyl series. 2,2′-Dinitro-6-carboxybiphenyl has a half-life of 125 minutes in boiling acetic acid (b.p. 118°); the 2′-methoxy analog has a half-life of 9 minutes at 25° in alcohol.[4] In the biphenyls the nitro group shows a larger interference effect than the methoxyl group. In the hindered amines the opposite results are found; N-succinyl-1-methylamino-2,4-dimethyl-6-nitrobenzene has a half-life of 36 minutes in boiling methyl acetate (b.p. 56°); the 6-methoxy analog has a half-life of 163 minutes in the same boiling solvent.

This can be explained on the basis of the reduced basicity of the amino group in the nitro compound, the increased double bond character of the carbon-nitrogen bond resulting in an increase in the ease of racemization.

The conclusion must be that the electronegativity as well as the size of the group must be considered in predicting the interference of a group when substituted ortho to the amino group.

Bibliography

1. Adams and Dankert, J. Am. Chem. Soc., **62**, 2191 (1940).
2. Adams and Stewart, *ibid.*, **63**, 2859 (1941).
3. Adams and Albert, *ibid.*, **64**, 1475 (1942).
4. Shriner, Adams and Marvel, Chapter 3 in Gilman's "Organic Chemistry," John Wiley and Sons, New York, (1938), p. 281.

VITA

The author was born in Ely, Minnesota, on February 3, 1914. He received his elementary education in the public schools of Ely, Minnesota, and Janesville, Wisconsin. He was graduated from the Memorial High School of Ely, Minnesota, in June, 1931. In September, 1937, he entered the University of Minnesota from which he received the degree of Bachelor of Chemistry in March, 1941. In the fall of 1941 he enrolled in the graduate school of the University of Illinois, where he held an organic chemistry assistantship for the first semester of the year 1941-1942, the Allied Chemical and Dye Corporation Fellowship during the second semester of the year 1941-1942 and during the period from June, 1943, to February, 1944, and the New York Community Trust Fellowship during the year 1942-1943.